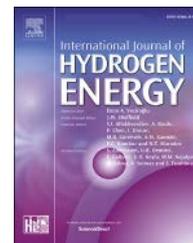


Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/ije

Short Communication

Fiber-shaped Co modified with Au and Pt crystallites for enhanced hydrogen generation from sodium borohydride

A. Zabielaite, A. Balciūnaitė, I. Stalnionienė, S. Lichušina, D. Šimkūnaitė, J. Vaičiūnienė, B. Šimkūnaitė-Stanyrienė, A. Selskis, L. Tamašauskaitė-Tamašiūnaitė*, E. Norkus

Center for Physical Sciences and Technology, Saulėtekio Ave. 3, Vilnius LT, 10257, Lithuania

ARTICLE INFO

Article history:

Received 8 March 2018

Received in revised form

4 October 2018

Accepted 23 October 2018

Available online 16 November 2018

Keywords:

Cobalt

Gold

Platinum

Borohydride

Hydrolysis

Hydrogen

ABSTRACT

This work presents the study of catalytic activity of the fiber-shaped Co decorated with low amounts of Au or Pt nanoparticles for the hydrolysis of sodium borohydride in alkaline conditions. The morphology, structure and composition of the prepared catalysts were examined using Field Emission Scanning Electron Microscopy, Energy Dispersive X-ray Analysis and Inductively Coupled Plasma Optical Emission Spectroscopy.

It was found that the decoration of the fiber-shaped Co with the Au or Pt nanoparticles allows enhancing of catalytic activity for the hydrolysis of sodium borohydride, compared with that of the pure fiber-shaped Co.

© 2018 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

On a global scale, hydrogen energy is being touted as an almost perfect strategy for mitigating energy and environmental challenges. Hydrogen is considered to be a clean and environmentally friendly energy source for the future, with wide-ranging applicability across heating, transportation, mechanical power, and electricity generation [1]. Eventually, hydrogen is expected to replace traditional energy storage and supply systems, or at least greatly reduce our dependence on them. Therefore, fundamental as well as technological

investigations concerning hydrogen generation have assumed great importance today.

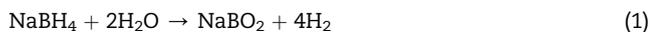
Sodium borohydride (NaBH_4) is one of the most promising candidates for these applications owing to its high theoretical hydrogen storage capacity (10.8 wt%), nontoxicity, high stability in strongly alkaline media under ambient operation conditions, and easily controllable hydrogen production [2–4]. Molecular hydrogen can be easily converted into energy by using PEM fuel cells thanks to its oxidation with air, giving water as the main by product [5]. The catalytic hydrolysis of NaBH_4 yields high-purity hydrogen and produces water-soluble discharge products [2]:

* Corresponding author.

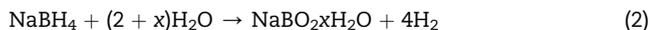
E-mail address: loreta.tamasauskaite@ftmc.lt (L. Tamašauskaitė-Tamašiūnaitė).

<https://doi.org/10.1016/j.ijhydene.2018.10.179>

0360-3199/© 2018 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.



However, in real conditions water should be taken into account since more water is needed to release 4 mol of hydrogen and can be expressed as:



where x is the excess of water. The rate of this reaction significantly depends on the catalyst used, its structure, and the selected support. In order to improve the NaBH_4 hydrolysis reaction many efforts have been made for developing of an efficient catalysts. The recent progresses in the development of the hydrogen generation from sodium borohydride hydrolysis are reviewed [2–4,6–10]. Conventionally, noble metals, such as Pt, Ru, Pd, or Rh have been found as the most effective catalysts for the hydrolysis of sodium borohydride [4,7,10–17]. Although noble metal catalysts maintain excellent catalytic activity and high stability for the NaBH_4 hydrolysis reaction, their high cost limits their wider use [4,6]. The necessity of finding more efficient, cost-effective and durable alternatives has led to further research. Development of catalyst systems based on the cheaper transition metals as a replacement for noble metal catalysts is highly desirable. A range of heterogeneous cobalt-based catalysts, such as Co, Co-B or Co-B doped with transition metals (Ni, Fe, Cu, Cr, Mn, Mo or W) have been studied [2,4,6–10,18–25]. They are thoroughly overviewed in comprehensive reviews [2,4,6–10]. Regardless tremendous efforts devoted for the development of the cobalt and cobalt-based catalyst with perfect catalytic activity, the major drawback is related to the deactivation of catalysts [9,26–30]. The catalysts surface during the reaction has been reported to be blocked by a thick passivation layer of B-O based compounds [27–29]. Promising way to reduce or even avoid the formation of adsorbed borates is development of binary or ternary cobalt-mixed systems with different metals. The developed Cu-Co based catalysts have demonstrated significant improvement in stability against adsorption of borates and subsequent deactivation of the catalyst [31]. The increased catalytic activity is deemed to be related to the electronic effects of the system. Moreover, in order to get the enhanced catalytic activity, the ternary and quaternary alloy catalysts such as Co-M-B and Co-P-B, and Co-M-B-P (where M = Ni, Cr, Mo, W, Mn, Cu, Ru) have been developed [9,32–42]. Significant improvement in the catalytic activity due to the synergic effect was observed. The best performance of this type of catalyst reported to date is a Co-Mn-B powder, giving a hydrogen generation rate (HGR) of $35,000 \text{ ml min}^{-1} (\text{g catalyst})^{-1}$ [35].

On the other hand, conventional heterogeneous catalysts are known to suffer from relatively low activities due to their limited exposed active sites. To enhance their activity, supports with a large surface area or dopants that effectively disperse the catalysts and increase their contact area with reactants are commonly employed. Recently graphene, graphene oxide or N-doped graphene hydrogel supported Co-Ni, Co-Pt, Co nanoparticles and CoBP [43–47], M@Co (M = Au, Ag, Fe) [48–53] have been also investigated.

However, enhancing the active surface area of the catalyst itself, without supporting it on other substrates or introducing

other elements is equally important, since the microstructures and surface morphologies play decisive roles in the catalytic performance. As compared to spherical catalysts, nanostructured catalysts contain more edges, corners, and faces, and consequently provide more active sites for catalytic reaction. Different nanostructured morphologies of Co-based catalysts have been developed so far. In particular, an array of Co films composed of mesoporous Co-B nanocatalysts with slit-like pores of different sizes [54], hollow spheres [55], flower-like [56], honeycomb-like [57] mesoporous Co-B structures and pompon-like Co-B nanoalloy [58] have been synthesized to improve the hydrolysis of NaBH_4 . The catalytic performance of all these nanocatalysts has been found to be significantly higher as compared to regular Co-B catalysts.

As was mentioned above, the shape and fine structure of the catalysts have important influence on catalytic properties. In addition, decoration of non-noble catalysts surfaces with small amount of noble metal nanoparticles can also enhance the same catalytic properties as well as to reduce the content of the expensive, noble metal in the catalytic system [4]. It is well known that a multimetallic system results in enhanced catalytic performance for hydrogen generation from NaBH_4 hydrolysis in comparison to a bimetallic system. In our previous study [49], we have demonstrated that the Co surface with a smooth structure, which was decorated with small amount of Au nanoparticles, showed improved catalytic activity for NaBH_4 hydrolysis, as compared to that of bare Co. Therefore, in the present study we use a fiber-like Co coating electroplated on a Cu surface as a substrate for deposition of Au or Pt crystallites (denoted as $\text{AuCo}_{\text{fiber}}/\text{Cu}$ and $\text{PtCo}_{\text{fiber}}/\text{Cu}$) with the aim to use them as catalysts to generate hydrogen from NaBH_4 solution. The prepared catalysts were examined using field-emission scanning electron microscopy (FESEM), energy-dispersive X-ray analysis (EDX), and inductively coupled plasma-optical emission spectroscopy (ICP-OES). Their catalytic activity was then evaluated for the hydrolysis of NaBH_4 in an alkaline medium.

Experimental

Chemicals

NaBH_4 (98%) $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (99.99%, $\geq 49.0\%$), H_2PtCl_6 (99.95%), $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (98%) and N-(2-Hydroxyethyl)ethylenediamine were purchased from Sigma-Aldrich Supply. H_2SO_4 (96%) and NaOH (99%) were purchased from Chempur Company. All chemicals were of analytical grade. Deionized water with the resistivity of $18.2 \text{ M}\Omega \text{ cm}^{-1}$ was used to prepare all the solutions.

Fabrication of catalysts

A fiber-shaped cobalt coating (approximately $3 \mu\text{m}$ thick) was electroplated on a $1 \times 1 \text{ cm}$ Cu foil. Prior to electrodeposition, the surface of the Cu foil was pretreated with SiC emery paper (grade 2500) and MgO powder, etched in 10% H_2SO_4 , and rinsed with deionized water. The Co coating was electroplated on the Cu foil using a solution containing $40 \text{ g}\cdot\text{L}^{-1}$ CoSO_4 , $100 \text{ g}\cdot\text{L}^{-1}$ NaOH, and $60 \text{ g}\cdot\text{L}^{-1}$ N-(2-Hydroxyethyl)ethylenediamine.

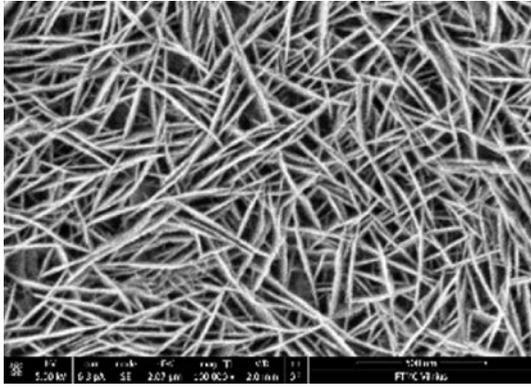


Fig. 1 – SEM view of the Co_{fiber} coating electroplated on the Cu surface from the solution containing $40 \text{ g}\cdot\text{L}^{-1} \text{CoSO}_4$, $100 \text{ g}\cdot\text{L}^{-1} \text{NaOH}$, and $60 \text{ g}\cdot\text{L}^{-1} \text{N-(2-Hydroxyethyl) ethylenediamine}$ at a current density of 20 mA cm^{-2} for 20 min at a temperature of $20 \pm 2 \text{ }^\circ\text{C}$.

Electrodeposition was performed using a galvanostatic control with a cathode current density of 20 mA cm^{-2} for 20 min at a temperature of $20 \pm 2 \text{ }^\circ\text{C}$.

Au or Pt crystallites were then deposited onto the Co-coated Cu electrodes by the galvanic displacement technique. For the deposition of Au crystallites, the Co electrodes were dipped into a $1 \text{ mM H AuCl}_4 + 0.1 \text{ M HCl}$ solution at a temperature of $25 \text{ }^\circ\text{C}$ for 30, 60, and 300 s [49]. For the deposition of Pt crystallites, the Co electrodes were dipped into a $1 \text{ mM H}_2\text{PtCl}_6 + 0.1 \text{ M HCl}$ solution at $25 \text{ }^\circ\text{C}$ for 10, 30, and 60 s.

Characterization of catalysts

The morphology and composition of the prepared catalysts were characterized using an SEM-focused ion beam facility (Helios Nanolab 650) equipped with an EDX spectrometer (INCA Energy 350 X-Max 20).

The Au, Pt, and Co metal loadings on the catalysts were estimated on the basis of ICP optical emission spectra recorded on an Optima 7000DV ICP optical emission spectrometer (Perkin Elmer).

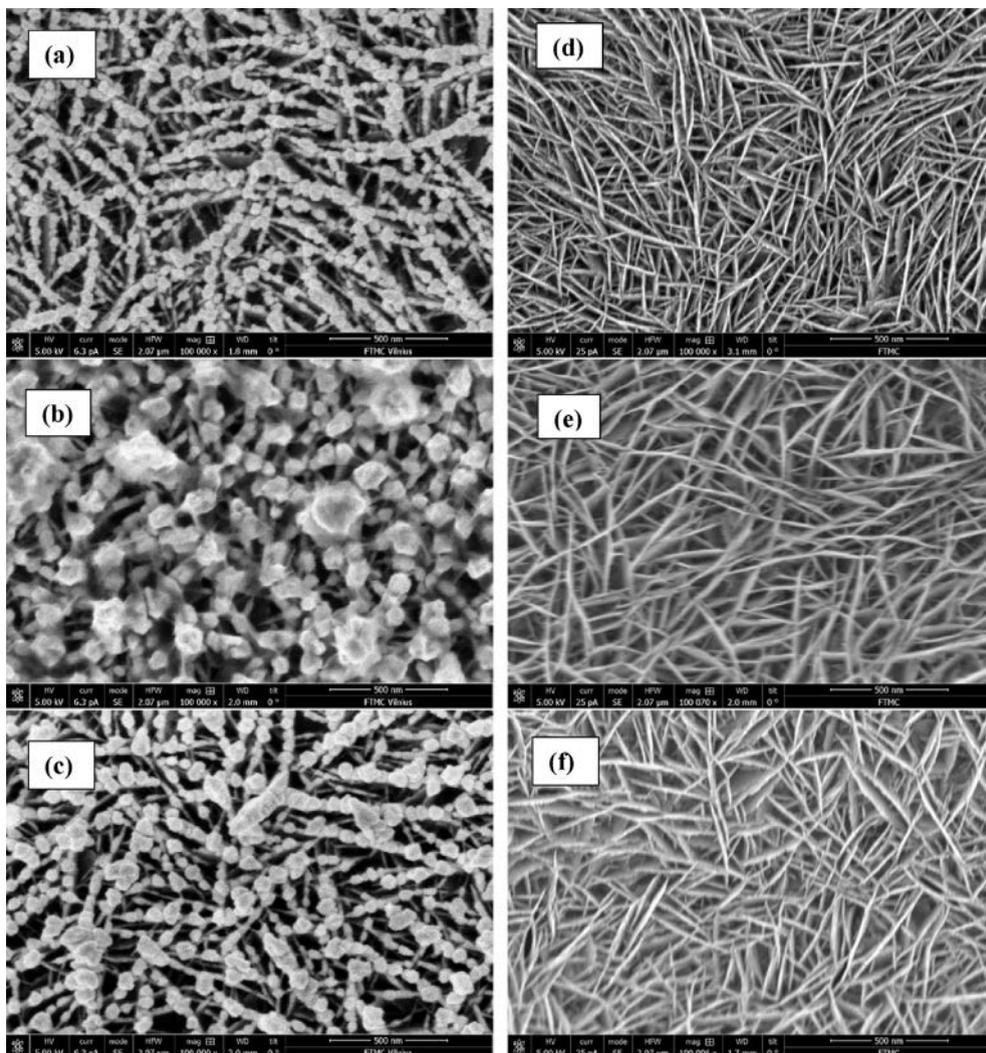


Fig. 2 – SEM images of $\text{AuCo}_{\text{fiber}}/\text{Cu}$ (a–c) and $\text{PtCo}_{\text{fiber}}/\text{Cu}$ (d–f) prepared by immersion of $\text{Co}_{\text{fiber}}/\text{Cu}$ in $1 \text{ mM H AuCl}_4 + 0.1 \text{ M HCl}$ for 30 (a), 60 (b) and 300 (c) s and $1 \text{ mM H}_2\text{PtCl}_6 + 0.1 \text{ M HCl}$ for 10 (d), 30 (e) and 60 (f) s.

Table 1 – Surface atomic composition of the Co_{fiber}/Cu and AuCo_{fiber}/Cu catalysts by EDX analysis. The catalysts are the same as in Figs. 1 and 2(a–c). The Au and Co loadings were determined by using ICP-OES.

Catalyst	t _{dep} of Au, s	Elements, at. %			Au loading, $\mu\text{g cm}^{-2}$	Co loading, $\mu\text{g cm}^{-2}$
		Au	Co	Cu		
Co _{fiber} /Cu	–	–	99.56	0.43	–	2353.0
AuCo _{fiber} /Cu	30	5.32	94.18	0.50	20.0	1615.5
	60	10.08	88.80	1.12	28.0	1550.0
	300	20.38	76.62	3.00	96.0	1002.5

Kinetic studies of the catalytic hydrolysis of NaBH₄

The amount of generated hydrogen was measured using a MilliGascounter (Type MGC-1 V3.2 PMMA, Ritter, Germany). In a typical measurement, a reaction solution containing NaBH₄ and NaOH was thermostated in an airtight flask, fitted with an outlet connected to the MilliGascounter for collecting evolved H₂ gas. The Co_{fiber}/Cu, AuCo_{fiber}/Cu, or PtCo_{fiber}/Cu catalysts were then immersed into the designated temperature solutions containing 5 wt% NaBH₄ + 0.4 wt% NaOH to initiate hydrolysis. The rate of hydrogen generation was measured at different solution temperatures (30–70 °C) to determine the activation energy.

Results and discussion

In the present study, the Au or Pt nanoparticle-modified fiber-shaped Co coating was investigated as a catalyst for hydrogen generation from NaBH₄ solution. The fiber-shaped Co coating was electroplated on a Cu surface and used as a sublayer for the deposition of Au or Pt crystallites.

As illustrated in Fig. 1, the Co coating consists of a layer of Co fibers in the order of tens of nanometers in thickness and hundreds of nanometers in length.

Fig. 2 shows SEM images of the Co_{fiber}/Cu modified with Au (a–c) and Pt (d–f) crystallites. Immersion of the Co_{fiber}/Cu electrodes into the 1 mM HAuCl₄ + 0.1 M HCl or 1 mM H₂PtCl₆ + 0.1 M HCl solutions for various time periods resulted in the deposition of Au and Pt crystallites on the respective fiber-shaped Co surfaces. EDX analysis data of the prepared Co_{fiber}/Cu, AuCo_{fiber}/Cu and PtCo_{fiber}/Cu catalysts are summarized in Tables 1 and 2. The Au and Pt loadings on the catalysts were determined by ICP-OES. As evident in Fig. 2, the

Table 2 – Surface atomic composition of the PtCo_{fiber}/Cu catalysts by EDX analysis. The catalysts are the same as in Fig. 2(d–f). The Pt and Co loadings were determined by using ICP-OES.

Catalyst	t _{dep} of Pt, s	Elements, at. %			Pt loading, $\mu\text{g cm}^{-2}$	Co loading, $\mu\text{g cm}^{-2}$
		Pt	Co	Cu		
PtCo _{fiber} /Cu	10	0.67	98.23	1.10	5.4	2745.0
	30	1.81	97.50	0.69	15.4	2473.5
	60	2.42	95.89	1.70	28.7	1982.5

Au nanoparticles appear as bright, cubic-shaped crystallites and are homogeneously dispersed on the fiber-shaped Co surface (Fig. 2 a–c). After immersing the Co_{fiber}/Cu electrode into the 1 mM HAuCl₄ + 0.1 M HCl solution for 30 and 60 s, Au crystallites sized 15–50 nm were deposited on the Co_{fiber}/Cu surface (Fig. 2 a,b). Immersion of the Co_{fiber}/Cu electrode into the 1 mM HAuCl₄ + 0.1 M HCl solution for 300 s resulted in the deposition of larger Au crystallites sized 30–100 nm (Fig. 2 c). The amounts of Au loadings on the catalysts were determined to be 20, 28, and 96 $\mu\text{g cm}^{-2}$ corresponding to immersion times of 30, 60 and 300 s (Table 1).

In the case of PtCo_{fiber}/Cu catalysts, Pt crystallites were not clearly seen in the SEM images (Fig. 2, d–f). However, their presence was confirmed by the results of EDX and ICP-OES analyses. The Pt loadings were 5.4, 14.4, and 28.7 $\mu\text{g cm}^{-2}$ corresponding to immersion times of 10, 30, and 60 s, respectively (Table 2).

Further, the activity of the Co_{fiber}/Cu, AuCo_{fiber}/Cu, and PtCo_{fiber}/Cu catalysts for the hydrolysis of NaBH₄ was investigated. Fig. 3 shows the volume of generated hydrogen with

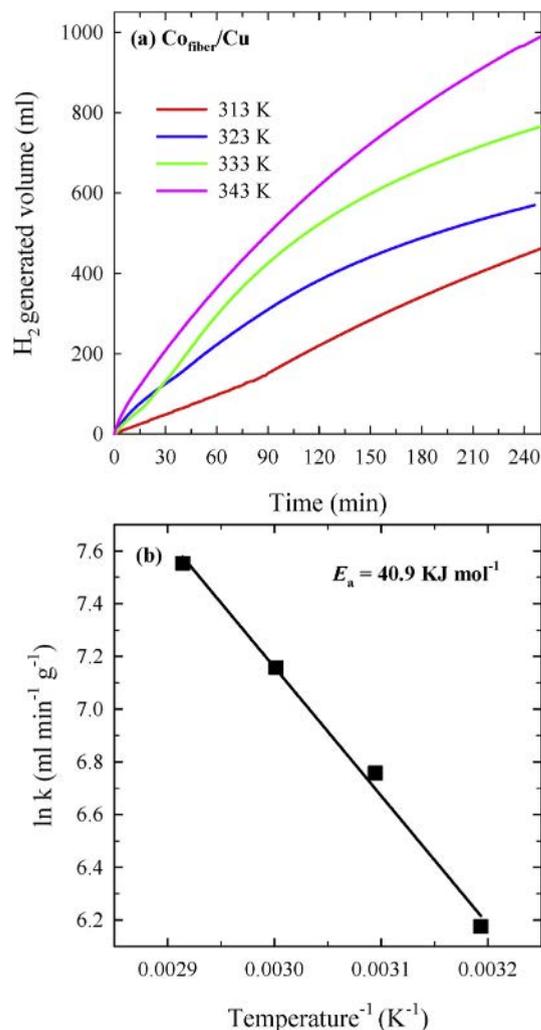


Fig. 3 – (a) H₂ generation from 15 ml 5 wt% NaBH₄ + 0.4 wt % NaOH catalyzed by the Co_{fiber}/Cu at different temperatures. (b) The Arrhenius plot calculated from the rates of NaBH₄ hydrolysis in a same solution.

Table 3 – Hydrogen generation rate obtained from 15 ml of 5 wt% NaBH₄ + 0.4 wt% NaOH solution catalyzed by the Co_{fiber}/Cu catalyst.

Catalysts	Co loading, $\mu\text{g cm}^{-2}$	Temperature, K	H ₂ generation rate, $\text{L min}^{-1} \text{g}_{\text{Co}}^{-1}$
Co _{fiber} /Cu	2353.0	313	0.4
		323	0.7
		333	1.1
		343	1.6

respect to reaction time catalyzed by Co_{fiber}/Cu in a 5 wt% NaBH₄ + 0.4 wt% NaOH solution at various temperatures. Data for the rate of hydrogen generation are summarized in Table 3. As seen from Table 3, the rate of catalytic hydrolysis of NaBH₄ in an alkaline medium exponentially increased with an increase in reaction temperature, and a maximum value of

1.6 L min⁻¹ g⁻¹ was obtained at a temperature of 70 °C. The temperature dependence of the rate of hydrogen generation can be expressed by the Arrhenius equation, as follows [59]:

$$k = Ae^{-E_a/RT} \quad (3)$$

where k is the rate constant, E_a is the activation energy (J), A is the frequency factor, and R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$). In order to find the values of E_a and A , an Arrhenius plot of $\ln(k)$ vs. $1/T$ was constructed from the data presented in Fig. 3a, as illustrated in Fig. 3b. An activation energy of 40.9 kJ mol^{-1} was calculated from this plot.

Hydrogen generation rates measured for the AuCo_{fiber}/Cu with Au loading of $28.0 \mu\text{g Au cm}^{-2}$ (a) and PtCo_{fiber}/Cu with Pt loading of $28.7 \mu\text{g Pt cm}^{-2}$ (c) catalysts at various temperatures are summarized in Fig. 4 and Table 4. In all cases, the rate of catalytic hydrolysis of NaBH₄ in alkaline conditions exponentially increased with increasing reaction temperature. The

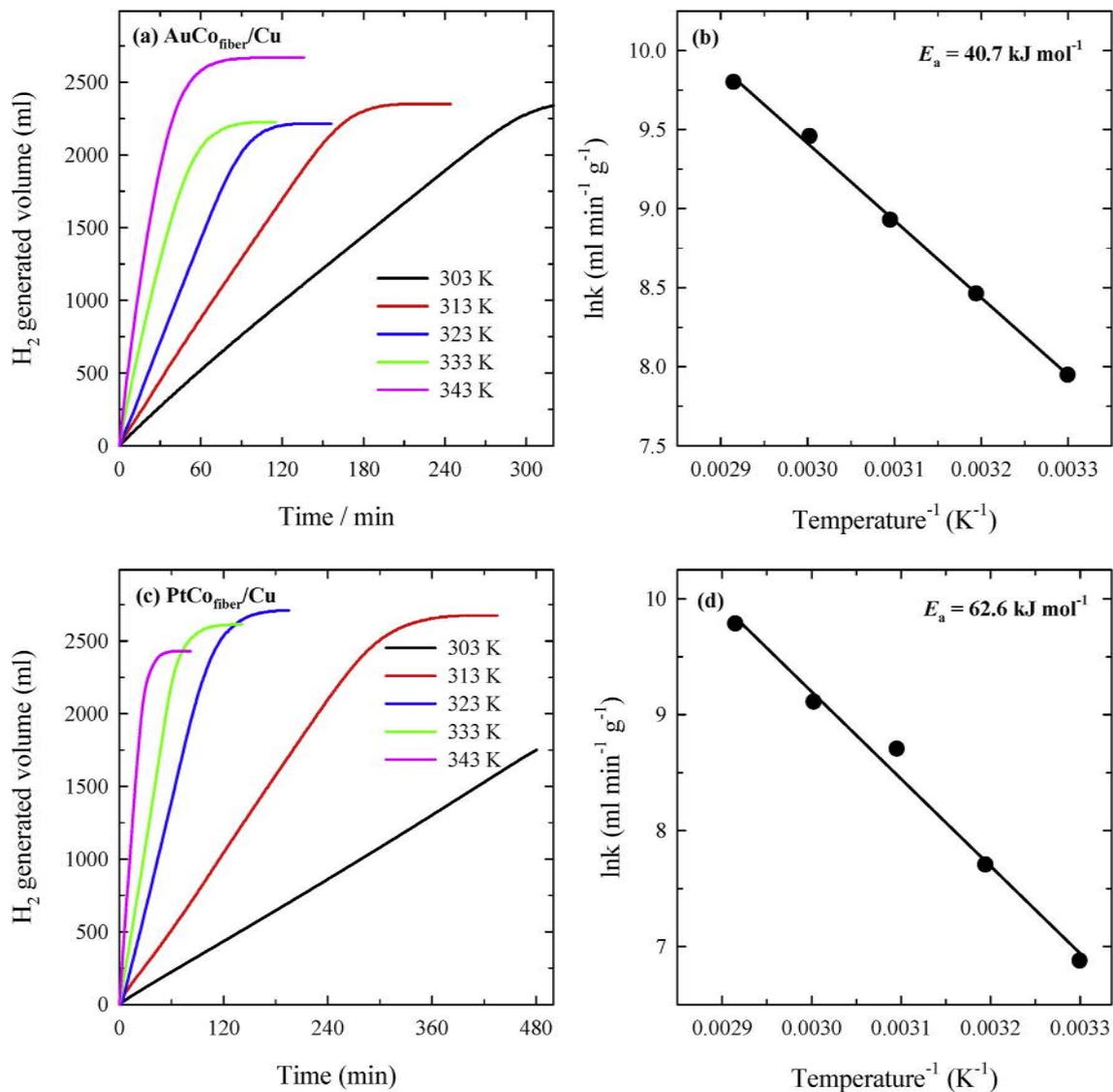


Fig. 4 – H₂ generation from 15 ml 5 wt% NaBH₄ + 0.4 wt% NaOH catalyzed by the AuCo_{fiber}/Cu with the Au loading of $28.0 \mu\text{g Au cm}^{-2}$ (a) and the PtCo_{fiber}/Cu catalyst with the Pt loading of $28.7 \mu\text{g Pt cm}^{-2}$ (c) at different temperatures. (b, d) The Arrhenius plot calculated from the rates of NaBH₄ hydrolysis in a same solution.

Table 4 – Hydrogen generation rate obtained from 15 ml of 5 wt% NaBH₄ + 0.4 wt% NaOH solution catalyzed by the different AuCo_{fiber}/Cu and PtCo_{fiber}/Cu catalysts.

Temperature, K	AuCo _{fiber} /Cu catalyst			PtCo _{fiber} /Cu catalyst		
	Au loading, $\mu\text{g cm}^{-2}$	H ₂ generation rate, $\text{L min}^{-1} \text{g}_{\text{Au}}^{-1}$	H ₂ generation rate, $\text{L min}^{-1} \text{g}_{\text{catalyst}}^{-1}$	Pt loading, $\mu\text{g cm}^{-2}$	H ₂ generation rate, $\text{L min}^{-1} \text{g}_{\text{Pt}}^{-1}$	H ₂ generation rate, $\text{L min}^{-1} \text{g}_{\text{catalyst}}^{-1}$
303	28.0	158.8	2.8	28.7	67.5	1.0
313		265.6	4.7		154.9	2.2
323		423.5	7.5		420.6	6.0
333		719.5	12.8		630.3	9.0
343		1012.3	17.9		1238.3	17.7
323	20.0	406.0	5.0	5.4	1155.4	2.3
323	96.0	132.9	11.6	15.4	600.6	3.7

Arrhenius plot calculated from the rates of NaBH₄ hydrolysis for these catalysts is shown in Fig. 4b and d. Based on these plots, activation energies were determined to be 40.7 kJ mol⁻¹ for the AuCo_{fiber}/Cu and 62.6 kJ mol⁻¹ for the PtCo_{fiber}/Cu catalysts. The E_a value for the Co_{fiber}/Cu and AuCo_{fiber}/Cu catalysts was lower than that obtained for Co (41.9 kJ mol⁻¹), Raney Co (53.7 kJ mol⁻¹) [60], and other catalysts reported in Ref. [21].

The hydrogen generation rate obtained for PtCo_{fiber}/Cu (28.7 $\mu\text{g Pt cm}^{-2}$) at a temperature of 70 °C was higher than that at AuCo_{fiber}/Cu (28 $\mu\text{g Au cm}^{-2}$) and totaled 1238.3 L min⁻¹ g_{Pt}⁻¹ and 1012.3 L min⁻¹ g_{Au}⁻¹, respectively.

Fig. 5 shows the rates of hydrogen generation from NaBH₄ solution when catalyzed by various AuCo_{fiber}/Cu and PtCo_{fiber}/Cu catalysts at 50 °C. Significantly higher hydrogen generation rates were obtained with the AuCo_{fiber}/Cu and PtCo_{fiber}/Cu catalysts (Table 4) as compared to those with Co_{fiber}/Cu (Table 3). Notably, the hydrogen generation rate also depended on the amount of Au or Pt loadings on the prepared catalysts. Comparing the performance of the AuCo_{fiber}/Cu catalysts in terms of the amount of Au loadings (ranging between 20 and 96 $\mu\text{g Au cm}^{-2}$) at a temperature of 50 °C, the maximum hydrogen generation rate of 423.5 L min⁻¹ g_{Au}⁻¹ was obtained at an Au loading of 28.0 $\mu\text{g Au cm}^{-2}$. In the case of PtCo_{fiber}/Cu catalysts with Pt loadings in the range 5–29 $\mu\text{g Pt cm}^{-2}$, the highest hydrogen generation rate of 1155.4 L min⁻¹ g_{Pt}⁻¹ at a temperature of 50 °C was obtained at the lowest amount of Pt loading (5.4 $\mu\text{g Pt cm}^{-2}$). For comparison, the hydrogen generation rates are also presented per grams of total Au-Co_{fiber} catalyst deposited on the Cu surface. The summarized data are given in Table 4. Hydrogen generation rates for all the obtained AuCo_{fiber}/Cu catalysts with different Au loading are ca. 11 times higher compared with those obtained for pure Co_{fiber}/Cu catalyst, whereas in the case of PtCo_{fiber}/Cu catalysts, the measured hydrogen generation rates depend on the Pt loadings and are ca. 5–11 times higher compared with those obtained for Co_{fiber}/Cu. It should be noted that the highest hydrogen generation rates at a temperature of 70 °C were obtained for the PtCo_{fiber}/Cu (28.7 $\mu\text{g Pt cm}^{-2}$) and AuCo_{fiber}/Cu (28 $\mu\text{g Au cm}^{-2}$) catalysts and totaled ca. 18 L min⁻¹ g_{catalyst}⁻¹. These results confirm that the fiber-shaped Co coatings decorated with Au or Pt crystallites efficiently catalyzed the hydrolysis of NaBH₄ in alkaline conditions.

Comparison of hydrogen evolution on catalysts prepared in this work with that obtained on various other catalysts

reported in the literature is summarized in Table 5. It is evident that the catalytic activity of the prepared AuCo_{fiber}/Cu and PtCo_{fiber}/Cu catalysts is higher as compared with those of the noble metal catalysts such as Pt/C, Pt/Si₃N₄, PtNi/Ni_{foam}, and non-noble metal-based catalysts: CoPt-PEDOT:PSS/MWCNT, Ni-Co/rGO, Co on 3D GO and Co-B [12,46,61–66].

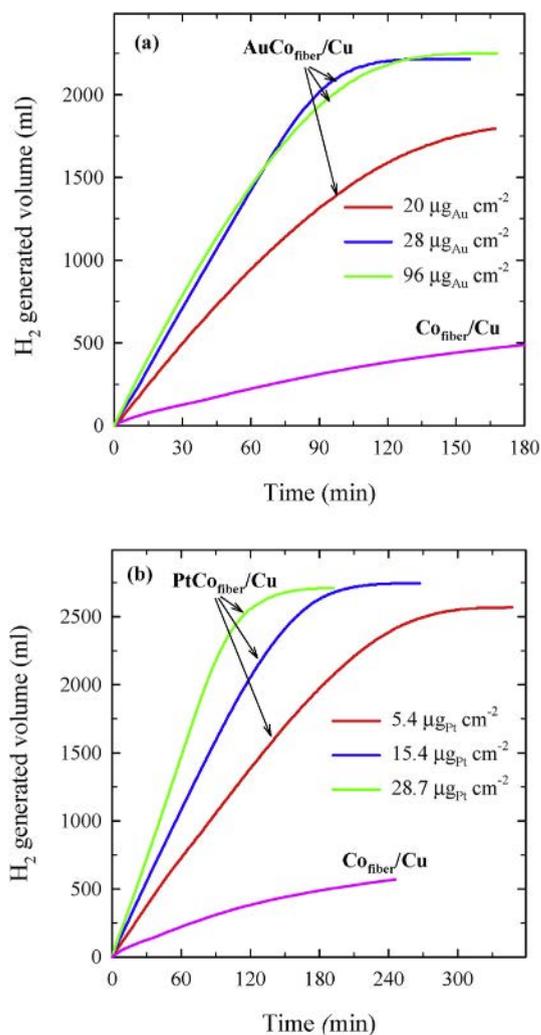
**Fig. 5 – H₂ generation from 15 ml 5 wt% NaBH₄ + 0.4 wt% NaOH at 50 °C catalyzed by the Co_{fiber}/Cu, AuCo_{fiber}/Cu and PtCo_{fiber}/Cu catalysts with different Au and Pt loadings.**

Table 5 – Comparison of hydrogen generation (HG) on various catalysts.

Catalyst	T, °C	HG	Reference
CoPt-PEDOT: PSS/MWCNT	25	6.9 L min ⁻¹ g ⁻¹	[61]
Ni-Co/r-GO		1.280 L min ⁻¹ g _{catalyst} ⁻¹	[62]
Co on 3DGO	25	4.394 L min ⁻¹ g _{cobalt} ⁻¹	[46]
Co-B	40	39.0 L min ⁻¹ g _{cobalt} ⁻¹	[63]
Pt/C	25	23.0 L min ⁻¹ g _{Pt} ⁻¹	[64]
PtNi/Ni _{foam}	70	75.7 L min ⁻¹ g _{Pt} ⁻¹	[65]
Pt/Si ₃ N ₄	80	24.2 L min ⁻¹ g _{Pt} ⁻¹	[12]
AuNiNPs	30	2.597 L min ⁻¹ g _{catalyst} ⁻¹	[66]
AuCo _{fiber} /Cu	30	158.8 L min ⁻¹ g _{Au} ⁻¹	This study
AuCo _{fiber} /Cu	30	2.8 L min ⁻¹ g _{catalyst} ⁻¹	This study
AuCo _{fiber} /Cu	70	1012.3 L min ⁻¹ g _{Au} ⁻¹	This study
AuCo _{fiber} /Cu	70	17.9 L min ⁻¹ g _{catalyst} ⁻¹	This study
PtCo _{fiber} /Cu	30	67.5 L min ⁻¹ g _{Pt} ⁻¹	This study
PtCo _{fiber} /Cu	70	1238.3 L min ⁻¹ g _{Pt} ⁻¹	This study
PtCo _{fiber} /Cu	70	17.7 L min ⁻¹ g _{catalyst} ⁻¹	This study

Conclusions

We have presented a simple method for the fabrication of efficient Co-based catalysts for NaBH₄ hydrolysis. A fiber-shaped Co coating was electroplated on a treated Cu surface, followed by deposition of Au or Pt crystallites on the Co coating by the galvanic displacement technique. The deposition of Au or Pt crystallites on the Co coating resulted in significantly enhanced catalytic activity for the hydrolysis of NaBH₄ in alkaline conditions, as compared to that of bare fiber-shaped Co coating. The highest hydrogen generation rates of 1238.3 L min⁻¹ g_{Pt}⁻¹ and 1012.3 L min⁻¹ g_{Au}⁻¹ were obtained for the PtCo_{fiber}/Cu and AuCo_{fiber}/Cu catalysts, respectively, at 70 °C, corresponding to Pt and Au loadings of 28.7 μg cm⁻² and 20.0 μg cm⁻².

Acknowledgment

This research was funded by a grant (No. M-ERA.NET-1/2016) from the Research Council of Lithuania.

REFERENCES

- [1] Rand DAJ, Dell RM. The hydrogen economy: a threat or an opportunity for lead-acid batteries? *J Power Sources* 2005;144:568–78.
- [2] Liu BH, Li ZP. A review: hydrogen generation from borohydride hydrolysis reaction. *J Power Sources* 2009;187:527–34.
- [3] Demirci UB, Miele P. Sodium borohydride versus ammonia borane, in hydrogen storage and direct fuel cell applications. *Energy Environ Sci* 2009;2:627–37.
- [4] Demirci UB, Akdim O, Andrieux J, Hannauer J, Chamoun R, Miele P. Sodium borohydride hydrolysis as hydrogen generator: issues, state of the art and applicability upstream from a fuel cell. *Fuel Cell* 2010;10:335–50.
- [5] Budroni MA, Garroni S, Mulas G, Rustici M. Bursting dynamics in molecular hydrogen generation via sodium borohydride hydrolysis. *J Phys Chem C* 2017;121:4891–8.
- [6] Muir SS, Yao X. Progress in sodium borohydride as a hydrogen storage material: development of hydrolysis catalysts and reaction systems. *Int J Hydrogen Energy* 2011;36:5983–97.
- [7] Retnamma R, Novais AQ, Rangel CM. Kinetics of hydrolysis of sodium borohydride for hydrogen production in fuel cell applications: a review. *Int J Hydrogen Energy* 2011;36:9772–90.
- [8] Demirci UB, Miele P. Reaction mechanisms of the hydrolysis of sodium borohydride: a discussion focusing on cobalt-based catalysts. *Compt Rendus Chem* 2014;17:707–16.
- [9] Patel N, Miotello A. Progress in Co-B related catalyst for hydrogen production by hydrolysis of boron-hydrides: a review and the perspectives to substitute noble metals. *Int J Hydrogen Energy* 2015;40:1429–64.
- [10] Brack P, Dann SE, Wijayantha KGU. Heterogeneous and homogenous catalysts for hydrogen generation by hydrolysis of aqueous sodium borohydride (NaBH₄) solutions. *Energy Sci. Engineer* 2015;3:174–88.
- [11] Sankir M, Semiz L, Serin RB, Sankir ND. Hydrogen generation from nanoflower platinum films. *Int J Hydrogen Energy* 2015;40:8522–9.
- [12] Lale A, Wasan A, Kumar R, Miele P, Demirci UB, Bernard S. Organosilicon polymer derived mesoporous 3D silicon carbide, carbonitride and nitride structures as platinum supports for hydrogen generation by hydrolysis of sodium borohydride. *Int J Hydrogen Energy* 2016;41:15477–88.
- [13] Cui X, Li H, Yu G, Yuan M, Yang J, Xu D, et al. Pt coated Co nanoparticles supported on N-doped mesoporous carbon as highly efficient, magnetically recyclable and reusable catalyst for hydrogen generation from ammonia borane. *Int J Hydrogen Energy* 2017;42:27055–65.
- [14] Olu P-Y, Bonnefont A, Braesch G, Martin V, Chatenet M. Influence of the concentration of borohydride towards hydrogen production and escape for borohydride oxidation reaction on Pt and Au electrodes – experimental and modelling insights. *J Power Sources* 2018;375:300–9.
- [15] Genç AE, Akça A, Kutlu B. The catalytic effect of the Au(111) and Pt(111) surfaces to the sodium borohydride hydrolysis reaction mechanism: a DFT study. *Int J Hydrogen Energy* 2018;43:14347–59.
- [16] Netskina OV, Kochubey DI, Prosvirin IP, Kellerman DG, Komova OV. Role of the electronic state of rhodium in sodium borohydride hydrolysis. *J Molec Catal A Chemicals* 2014;390:125–32.
- [17] Wei Y, Wang Y, Wei L, Zhao X, Liu H. Highly efficient and reactivated electrocatalyst of ruthenium electrodeposited on nickel foam for hydrogen evolution from NaBH₄ alkaline solution. *Int J Hydrogen Energy* 2018;43:592–600.
- [18] Vinokurov V, Stavitskaya A, Glotov A, Ostudin A, Lvov Y. Halloysite nanotube-based cobalt mesocatalysts for hydrogen production from sodium borohydride. *J Solid State Chem* 2018;268:182–9.
- [19] Chen B, Chen S, Bandal HA, Appiah-Ntiamoah R, Jadhav AR, Kim H. Cobalt nanoparticles supported on magnetic core-shell structured carbon as a highly efficient catalyst for hydrogen generation from NaBH₄ hydrolysis. *Int J Hydrogen Energy* 2018;43:9296–306.
- [20] Wang X, Liao J, Li H, Wang H, Ji S. Highly active porous Co-B nanoalloy synthesized on liquid-gas interface for hydrolysis of sodium borohydride. *Int J Hydrogen Energy* 2018;43:17543–55.
- [21] Wang Y, Li T, Bai S, Qi K, Cao Z, Zhang K, et al. Catalytic hydrolysis of sodium borohydride via nanostructured cobalt-boron catalysts. *Int J Hydrogen Energy* 2016;41:276–84.
- [22] Wang X, Liao J, Li H, Wang H, Wang R. Preparation of pompon-like Co-B nanoalloy by a room-temperature solid-

- state-reaction as a catalyst for hydrolysis of borohydride solution. *Int J Hydrogen Energy* 2017;42:6646–56.
- [23] Wang X, Liao J, Li H, Wang H, Ji S. Highly active porous Co-B nanoalloy synthesized on liquid-gas interface for hydrolysis of sodium borohydride. *Int J Hydrogen Energy* 2018;43:17543–55.
- [24] Wang L, Zhong M, Li J, Zhao X, Hao W, Guo Y. Highly efficient ferromagnetic Co-B-O catalyst for hydrogen generation. *Int J Hydrogen Energy* 2018;43:17164–71.
- [25] Guo J, Hou Y, Li B, Liu Y. Novel Ni-Co-B hollow nanospheres promote hydrogen generation from the hydrolysis of sodium borohydride. *Int J Hydrogen Energy* 2018;43:15245–54.
- [26] Demirci UB, Miele P. Cobalt-based catalysts for the hydrolysis of NaBH₄ and NH₃BH₃. *Phys Chem Chem Phys* 2014;16:6872–85.
- [27] Akdim O, Demirci UB, Miele P. Deactivation and reactivation of cobalt in hydrolysis of sodium borohydride. *Int J Hydrogen Energy* 2011;36:13669–75.
- [28] Arzac GM, Rojas TC, Fernández A. Boron compounds as stabilizers of a complex microstructure in a Co-B-based catalyst for NaBH₄ hydrolysis. *ChemCatChem* 2011;3:1305–13.
- [29] Arzac GM, Hufschmidt D, Jiménez de Haro MC, Fernández A, Sarmiento B, Jiménez MA, et al. Deactivation, reactivation and memory effect on Co-B catalyst for sodium borohydride hydrolysis operating in high conversion conditions. *Int J Hydrogen Energy* 2012;37:14373–81.
- [30] Paladini M, Arzac GM, Godinho V, Hufschmidt D, Jiménez de Haro MC, Beltrán AM, et al. The role of cobalt hydroxide in deactivation of thin film Co-based catalysts for sodium borohydride hydrolysis. *Appl Catal B Environ* 2017;210:342–51.
- [31] Eugénio S, Demirci UB, Silva TM, Carmezim MJ, Montemor MF. Copper-cobalt foams as active and stable catalysts for hydrogen release by hydrolysis of sodium borohydride. *Int J Hydrogen Energy* 2016;41:8438–48.
- [32] Dai HB, Liang Y, Wang P, Yao XD, Rufford T, Lu M, et al. High-performance cobalt-tungsten-boron catalyst supported on Ni foam for hydrogen generation from alkaline sodium borohydride solution. *Int J Hydrogen Energy* 2008;33:4405–12.
- [33] Fernandes R, Patel N, Miotello A. Efficient catalytic properties of Co-Ni-P-B catalyst powders for hydrogen generation by hydrolysis of alkaline solution of NaBH₄. *Int J Hydrogen Energy* 2009;34:2893–900.
- [34] Fernandes R, Patel N, Miotello A, Calliari L. Co-Mo-B-P alloy with enhanced catalytic properties for H₂ production by hydrolysis of ammonia borane. *Top Catal* 2012;55:1032–9.
- [35] Yuan X, Jia C, Ding X-L, Ma Z-F. Effects of heat-treatment temperature on properties of cobalt-manganese-boride as efficient catalyst toward hydrolysis of alkaline sodium borohydride solution. *Int J Hydrogen Energy* 2012;37:995–1001.
- [36] Fernandes R, Patel N, Paris A, Calliari L, Miotello A. Improved H₂ production rate by hydrolysis of ammonia borane using quaternary alloy catalysts. *Int J Hydrogen Energy* 2013;38:3313–22.
- [37] Zhuang D-W, Kang Q, Muir SS, Yao X, Dai H-B, Ma G-L, et al. Evaluation of a cobalt-molybdenum-boron catalyst for hydrogen generation of alkaline sodium borohydride solution-aluminum powder system. *J Power Sources* 2013;224:304–11.
- [38] Wang W, Zhao Y, Chen D, Wang X, Peng X, Tian J. Promoted Mo incorporated Co-Ru-B catalyst for fast hydrolysis of NaBH₄ in alkaline solutions. *Int J Hydrogen Energy* 2014;39:16202–11.
- [39] Wang Y, Li G, Wu S, Wei Y, Meng W, Xie Y, et al. Hydrogen generation from alkaline NaBH₄ solution using nanostructured Co-Ni-P catalysts. *Int J Hydrogen Energy* 2017;42:16529–37.
- [40] Wei Y, Meng W, Wang Y, Gao Y, Zhang K. Fast hydrogen generation from NaBH₄ hydrolysis catalyzed by nanostructured Co-Ni-B catalysts. *Int J Hydrogen Energy* 2017;42:6072–9.
- [41] Zou Y, Yin Y, Gao Y, Xiang C, Chu H, Qiu S, et al. Chitosan-mediated Co-Ce-B nanoparticles for catalyzing the hydrolysis of sodium borohydride. *Int J Hydrogen Energy* 2018;43:4912–21.
- [42] Sun H, Meng J, Jiao L, Cheng F, Chen J. A review of transition-metal boride/phosphide-based materials for catalytic hydrogen generation from hydrolysis of boronhydrides. *Inorg Chem Front* 2018;5:760–72.
- [43] Saha S, Ganguly S, Banerjee D, Kargupta K. Novel bimetallic graphene-cobalt-nickel (GCo-Ni) nano-ensemble electrocatalyst for enhanced borohydride oxidation. *Int J Hydrogen Energy* 2015;40:1760–73.
- [44] Saha S, Basak V, Dasgupta A, Ganguly S, Banerjee D, Kargupta K. Graphene supported bimetallic G-Co-Pt nanohybrid catalyst for enhanced and cost effective hydrogen generation. *Int J Hydrogen Energy* 2014;39:11566–77.
- [45] Tamašauskaitė-Tamašiūnaitė L, Radomskis A, Antanavičiūtė K, Jablonskienė J, Balčiūnaitė A, Žieliene A, et al. Graphene supported platinum-cobalt nanocomposites as electrocatalysts for borohydride oxidation. *Int J Hydrogen Energy* 2014;39:4282–90.
- [46] Wang J, Ke D, Li Y, Zhang H, Han S. Efficient hydrolysis of alkaline sodium borohydride catalyzed by cobalt nanoparticles supported on three-dimensional graphene oxide. *Mater. Research Bull* 2017;95:204–10.
- [47] Men Y, Su J, Du X, Liang L, Luo W. CoBP nanoparticles supported on three-dimensional nitrogen-doped graphene hydrogel and their superior catalysis for hydrogen generation from hydrolysis of ammonia borane. *J Alloy Comp* 2018;735:1271–6.
- [48] Pei F, Wang Y, Wang X, He P, Chen Q, Wang X, et al. Performance of supported Au-Co alloy as the anode catalyst of direct borohydride-hydrogen peroxide fuel cell. *Int J Hydrogen Energy* 2010;35:8136–42.
- [49] Tamašauskaitė-Tamašiūnaitė L, Jagminienė A, Balčiūnaitė A, Zabelaitė A, Žieliene A, Naruskevicius L, et al. Electrocatalytic activity of the nanostructured Au-Co catalyst deposited onto titanium towards borohydride oxidation. *Int J Hydrogen Energy* 2013;38:14232–41.
- [50] Guo L-T, Cai Y-Y, Ge J-M, Zhang Y-N, Gong L-H, Li X-H, et al. Multifunctional Au-Co@CN nanocatalyst for highly efficient hydrolysis of ammonia borane. *ACS Catal* 2015;5:388–92.
- [51] Du C, Su J, Luo W, Cheng G. Graphene supported Ag@Co core-shell nanoparticles as efficient catalysts for hydrolytic dehydrogenation of amine boranes. *J Molec Catal A Chemicals* 2014;383–384:38–45.
- [52] Ai L, Liu X, Jiang J. Synthesis of loofah sponge carbon supported bimetallic silver-cobalt nanoparticles with enhanced catalytic activity towards hydrogen generation from sodium borohydride hydrolysis. *J Alloy Comp* 2015;625:164–70.
- [53] Tsai CW, Chen HM, Liu RS, Lee J-F, Chang SM, Weng BJ. Magnetically recyclable Fe@Co core-shell catalysts for dehydrogenation of sodium borohydride in fuel cells. *Int J Hydrogen Energy* 2012;37:3338–43.
- [54] Gupta S, Patel N, Fernandes R, Kothari DC, Miotello A. Mesoporous Co-B nanocatalyst for efficient hydrogen

- production by hydrolysis of sodium borohydride. *Int J Hydrogen Energy* 2013;38:14685–92.
- [55] Ma H, Ji W, Zhao J, Liang J, Chen J. Preparation, characterization and catalytic NaBH₄ hydrolysis of Co-B hollow spheres. *J Alloy Comp* 2008;474:584–9.
- [56] Tong DG, Han X, Chu W, Chen H, Ji XY. Preparation and characterization of Co-B flowers with mesoporous structure. *Mater Res Bull* 2008;43:1327–36.
- [57] Tong DG, Chu W, Wua P, Zhanga L. Honeycomb-like Co-B amorphous alloy catalysts assembled by a solution plasma process show enhanced catalytic hydrolysis activity for hydrogen generation. *RSC Adv* 2012;2:2369–76.
- [58] Wang X, Liao J, Li H, Wang H, Wang R. Preparation of pompon-like Co-B nanoalloy by a room-temperature solid-state-reaction as a catalyst for hydrolysis of borohydride solution. *Int J Hydrogen Energy* 2017;42:6646–56.
- [59] Arrhenius SA. Über die dissociationswärme und den einfluss der temperatur auf den dissociationsgrad der electrolyte. *Z Phys Chem* 1889;4:96–116.
- [60] Liu BH, Li ZP, Suda S. Nickel- and cobalt-based catalysts for hydrogen generation by hydrolysis of borohydride. *J Alloy Comp* 2006;415:288–93.
- [61] Wang X, Zhao Y, Peng X, Wang J, Jing C, Tian J. Synthesis and characterizations of CoPt nanoparticles supported on poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) functionalized multi-walled carbon nanotubes with superior activity for NaBH₄ hydrolysis. *Mater Sci Eng, B* 2015;200:99–106.
- [62] Chou C-C, Hsieh C-H, Chen B-H. Hydrogen generation from catalytic hydrolysis of sodium borohydride using bimetallic Ni-Co nanoparticles on reduced graphene oxide as catalysts. *Energy* 2015;90:1973–82.
- [63] Akdim O, Demirci UB, Muller D, Miele P. Cobalt (II) salts, performing materials for generating hydrogen from sodium borohydride. *Int J Hydrogen Energy* 2009;38:2631–7.
- [64] Bai Y, Wu C, Wu F, Yi B. Carbon-supported platinum catalysts for on-site hydrogen generation from NaBH₄ solution. *Mater Lett* 2006;60:2236–9.
- [65] Tamašauskaitė-Tamašiūnaitė L, Zabielaite A, Balčiūnaitė A, Šebeka B, Stalnionienė I, Buzas V, et al. Deposition of Pt nanoparticles on Ni foam via galvanic displacement. *J Electrochem Soc* 2017;164:D53–6.
- [66] Wang X, Sun S, Huang Z, Zhang H. Preparation and catalytic activity of PVP-protected Au/Ni bimetallic nanoparticles for hydrogen generation from hydrolysis of basic NaBH₄ solution. *Int J Hydrogen Energy* 2014;39:905–16.